

S P E C I F I C A T I O N

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN that Todd M. Baranek, resident of Columbus, State of Ohio, and citizen of the United States of America, have invented certain new and useful improvements in a

**HIGH DENSITY METAL OXIDE FILLERS IN RUBBER COMPOUNDS**

of which the following is a specification.

**HIGH DENSITY METAL OXIDE FILLERS IN RUBBER COMPOUNDS**

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**FIELD OF THE INVENTION**

This invention relates to the use of high density metal oxide fillers in rubber compounds.

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**BACKGROUND OF THE INVENTION**

Rubber compounds have progressed from the use of untreated natural rubber to enormously complex polymeric systems, formulated with synthetic elastomeric polymers for such specific uses as vehicle tires, vibration dampers, and other products.

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Early in the development of sophisticated rubber products, compounders of rubber products dispersed fillers into various polymers as a means of both providing physical reinforcement and bulk to the elastomeric polymer. Carbon black was the first material commonly used as a filler. Later, silica has become a preferred filler, both alone and in combination with carbon black. Use of silica fillers improves rubber properties such as reducing rolling resistance (measured using polymer physics properties such as hysteresis), increasing road traction (particularly on wet surfaces), and enhancing other properties vital to improved fuel economy for vehicles, whose tires are engineered with tread compounds including such fillers.

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While silica-containing rubber compounds have become preferred for tread compounds, the search in the art continues for other materials that can improve these vital vehicle tire performance properties. Consumers, governments, and vehicle manufacturers demand ever-better vehicle tire performance. Tire manufacturers strain to reduce costs of meeting customer expectations.

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**SUMMARY OF THE INVENTION**

What the art needs is another class of fillers for rubber compounding that can be used at least in vehicle tire tread compounding as a substitute for, or an enhancement to, conventional tire fillers, in order to further improve vehicle tire performance at potentially lower costs of manufacture.

Moreover, this need in the art generally exists for any rubber compound which may require specific viscoelastic performance properties that are currently unavailable in commercial rubber compounds. For example, nearly all rubber compounds can benefit from an extension of filler choices in unexpected directions, once the demonstration of specific viscoelastic performance properties is known to those specific rubber compounders for their own specific rubber products.

The present invention solves the problems in the art by providing another class of fillers which can improve rubber compounds ranging from vehicle tire components to rubber hoses to vibration dampers.

One aspect of the present invention is a method of using high density metal oxide fillers in rubber compounds, comprising the steps of (a) selecting a high density metal oxide filler according to its specific performance properties, and (b) introducing the filler into rubber polymers for subsequent mixing to create a vulcanizable rubber compound.

Another aspect of the present invention is a vulcanizable rubber compound, comprising at least one elastomer, including but not limited to natural or synthetic rubber, or blends thereof, and at least one high density metal oxide filler.

Another aspect of the present invention is a vehicle tire component made from the vulcanizable rubber compound identified in the paragraph above. Another aspect of the present invention is a vehicle tire comprising at least the vehicle tire component identified above.

Another aspect of the present invention is a method of vulcanizing the rubber compound above, comprising the steps of mixing at least one elastomer, comprising a natural or synthetic rubber, and at least one high density metal oxide filler and polymerizing the rubber monomer.

A feature of the invention is the use of a high density metal oxide filler that replaces or augments conventional reinforcement fillers in rubber compounds in a manner that utilizes viscoelastic performance properties of the rubber compound for a specific end use.

An advantage of the invention is the ability of one skilled in the art to select a high density metal oxide filler according to its viscoelastic performance properties for a specific rubber compound for a specific use.

Another advantage of the invention is the possible reduction of cost of manufacture of the rubber compound by reducing the amount of expensive silica coupling agents which conventional silica-filled rubber compounds invariably contain by the reduction of silica required in the rubber compound. Preferably, this reduction aims toward elimination of silica as a reinforcing filler.

"Metal oxide filler" means a chemical composition of a metal and an oxide, where the metal is selected from Groups IVA, VA, IB, VIB, VIIB and VIIIB metals, and reacted with oxygen.

"High density" means a specific gravity of greater than about 5.7 g/cm<sup>3</sup> and preferably greater than about 6.5 g/cm<sup>3</sup> and most preferably greater than about 8 g/cm<sup>3</sup>.

Other features and advantages of invention will be disclosed in conjunction with an explanation of the embodiments of the invention in conjunction with the following drawings.

#### BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a graph of MTS Tangent Delta Values for two examples of the invention in comparison with a prior art compound.

Fig. 2 is a graph of Zwick Rebound Values for two examples of the invention in comparison with a prior art compound.

Fig. 3 is a graph of MTS Tangent Delta Values for two other examples of the invention in comparison with a second prior art compound.

Fig. 4 is a graph of Zwick Rebound Values for two other examples of the invention in comparison with a second prior art compound.

#### DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

##### Elastomers for Rubber Compounds

Any conventionally used elastomer for rubber compounding is potentially available for the advantages of the present invention arising from the use of high density metal oxide filler therewith.

- Non-limiting examples of elastomers potentially useful in the present invention include the following, individually as well as in combination, according to the desired final viscoelastic properties of the rubber compound: Natural Rubber (*Hevea* and *Guayule*), Polyisoprene Rubber, Styrene Butadiene Rubber,  
5 Polybutadiene Rubber, Butyl Rubbers, Halobutyl Rubbers, Ethylene Propylene Rubbers, Crosslinked Polyethylene, Neoprenes, Nitrile Rubbers, Chlorinated Polyethylene Rubbers, Silicone Rubbers, Specialty Heat & Oil Resistant Rubbers, Other Specialty Rubbers, and Thermoplastic Rubbers, as such terms are employed in The Vanderbilt Rubber Handbook, Thirteenth Edition, (1990).
- 10 Preferred elastomers include natural rubber, isoprene, styrene-butadiene copolymers, and butadiene rubber because of their common usage in the tire industry.

The ratios (often expressed as adding up to 100 parts) of such polymer blends can range across the broadest possible range according to the need of final viscoelastic properties desired for the polymerized rubber compound. One skilled in the art, without undue experimentation, can readily determine which elastomers 15 in what amount is appropriate for a resulting desired viscoelastic property range, which can then be improved by the selection of the novel fillers according the teachings of the present invention. For example, one skilled in the art need only 20 to look to the vast body of patent literature on rubber compounding as used in the vehicle tire industry to find suitable combinations and amounts of elastomers for preparation of vulcanizable rubber compounds for a variety of rubber components assembled into an uncured (so-called "green") tire for final vulcanization that cures the tire by crosslinking, principally using sulfur crosslinks.

25 More specifically, the tire industry often selects styrene and butadiene copolymers in ratios ranging from about 0 percent styrene to about 80 percent styrene, and preferably from about 0 to about 45 percent styrene for rubber tire tread compounds. Tread compounds are near the top of any list for viscoelastic performance properties because of the road contact such compounds have and the 30 balance of rolling resistance and traction on wet, ice and snow covered surfaces such rubber compounds should have.

Commercially available sources for natural rubber and synthetic rubber are very well known to those skilled in the art, but special mention is given to Firestone Polymers of Akron, Ohio, USA as a source of both natural rubber in latex form and synthetic polymers used in the rubber industry.

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#### High Density Metal Oxide Filler

According to the definitions of High Density and Metal Oxide above, the selection of novel fillers according to the present invention is based on desired viscoelastic performance properties.

10 Expressed as an empirical formula, such high density metal oxides can be:

- I.  $M_n(O)_{2n}$
- II.  $M_n(O)_{3n/2}$
- III.  $(M_1)_n(M_2)_n(O)_{2n}$

where M is a metal selected from Groups IVA, VA, IB, VIB, VIIB and VIIIB metals; O is oxygen; and n is the valence of the metal.

15 Non-limiting examples of high density metal oxide compositions include bismuth oxides, phosphorous oxides, tin oxides, copper oxides, and iron/manganese tungsten oxides. Depending on the valence of the metal involved, there can be multiple oxide candidates for a given metal.

20 Preferably, the filler is bismuth trioxide.

The amount of high density metal oxide filler to be mixed into the vulcanizable rubber compound depends on the presence or absence of other fillers, as well as the desired physical properties of the resulting compound. The amount of metal oxide filler ranges from about 0 to about 150 phr, and preferably from 25 about 5 to about 80 phr (parts per hundred rubber -- where "hundred rubber" means 100 parts of elastomer(s)).

30 High density metal oxides are fine chemicals commercially available from numerous sources. The use of Internet, Chemical Catalogs, and Technical Literature will quickly reveal such sources. Special mention is made of The Shepherd Chemical Company of Cincinnati, Ohio, USA; the American International Chemical Company of Natick, Massachusetts, USA; and Atomix, Inc. of Hohokus, New Jersey, USA as sources of bismuth trioxide.

Additional and Optional Ingredients

The sophistication of rubber chemistry has developed a vast body of choices for one skilled in the art to select elastomers, fillers, curing packages, processing aids, antioxidants and antiozonants, coupling agents, and the like. Without undue experimentation and utilizing the patent and technical literature, one skilled in the art can develop a variety of specific vulcanizable rubber compounds for subsequent construction and vulcanization according to the specific rubber product desired.

For example, without limitation, a tire tread compound typically also contains elastomers, fillers, processing oils/aids, antidegradants, zinc oxide, stearic acid, sulfur, accelerators and coupling agents. Such compound can have such additional ingredients in the following amounts:

fillers: from about 0 to about 150 phr, and preferably from about 30 to about 80 phr;

processing oils/aids: from about 0 to about 75 phr, and preferably from about 0 to about 40 phr;

antidegradants: from about 0 to about 10 phr, and preferably from about 0 to about 5 phr;

stearic acid: from about 0 to about 5 phr, and preferably from about 0 to about 3phr;

zinc oxide: from about 0 to about 10 phr, and preferably from about 0 to about 5 phr;

sulfur: from about 0 to about 10 phr, and preferably from about 0 to about 4 phr;

accelerators: from about 0 to about 10 phr, and preferably from about 0 to about 5 phr; and

coupling agent: from about 0 to about 30 phr, and preferably from about 5 to about 15 phr.

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Method of Making Vulcanizable Rubber Compound

In the more than 100 years of rubber compounding of tires for the automobile industry, very sophisticated and capital intensive equipment has been

built to produce such rubber products at the lowest possible cost. However, such rubber products can also be produced on the bench scale or in pilot plants. Therefore, one skilled in the art has another vast variety of choices to make the rubber compound for subsequent vulcanization.

5        Specifically, without limitation, an open mill or Banbury type mixer is usually employed to mix the elastomeric ingredients, the fillers, the additives, etc. Such mixing usually occurs in stages, during which ingredients may or may not be added. In the case of mixing a tire tread compound, typically the mixing process is comprised of a masterbatch initial mixing stage, followed by additional non-productive mixing stage(s), and ending with a final, productive (curative containing) mixing stage.

10      Typically, ingredients such as elastomers, fillers, oils and processing aids, antioxidants and antiozonants, zinc oxide and stearic acid, are added during the initial masterbatch. The initial masterbatch may be followed by another masterbatch, in which additional fillers and additives are added, or a non-productive mix stage in which no ingredients are added. Non-productive mix stages during which no ingredients are added may be used to further disperse fillers and other ingredients within the elastomer, or to decrease the viscosity of the mixed rubber compound.

15      20     A final mixing stage is then employed, during which curatives, including accelerators, and additional processing aids and antioxidants/antiozonants may be added. This final mix may also be followed by a non-productive mixing stage in which no ingredients are added. Again, one skilled in the art should not have the need for undue experimentation to select the most appropriate type of mixing to achieve a vulcanizable rubber compound according to the present invention.

#### Method of Assembly and Crosslinking the Rubber Compound

The rubber and tire industry has developed manual, semi-automated, and fully-automated means of manufacturing rubber products.

25      30     In the case of vehicle tires, the means are usually semi-automated and well documented in the literature. Multiple types of different rubber compounds (sidewall rubbers, innerliner rubbers, bead filler rubbers, body ply rubbers, skim stock rubbers and tread rubbers) are assembled along with rubber-coated metal

beads and metal plies to form a conventional vehicle tire. The selection of specific metal alloys and elastomeric compounds, and the configuration and dimensions of the various metallic and elastomeric components is also well understood by those skilled in the art of tire building.

5       The assembly of the rubber "green" tire is followed by curing in a press mold to concurrently crosslink the elastomeric components and mold the elastomeric components into a final tire. Vulcanization techniques are also well known.

10      The assembly and final production steps of other rubber products are also well known. One skilled in the art can readily find such information in the paper and electronic literature.

#### Usefulness of the Invention

15      The selection of a high density metal oxide filler to reduce or eliminate the use of conventional fillers in rubber compounds produces unexpected viscoelastic properties.

20      In the art of rubber compounding for the tire industry, certain physical tests of the rubber compound are used as predictors of cured tire properties. Tangent  $\delta$  at 0°C is an indicator of wet traction, such that increases in tangent  $\delta$  at 0°C correlate to improved wet traction of a cured tread compound. Tangent  $\delta$  at 65°C is a predictor of rolling resistance, such that lower results when compared to a control are indicative of decreased rolling resistance. Percent rebound at both 0°C and 65°C are predictors of wet traction and rolling resistance of the tread compound, as well. Lower percent rebound of a compound at 0°C, when compared to a control, is indicative of increased hysteresis, which corresponds to increased wet traction properties. Likewise, increased percent rebound at 65°C when compared to a control compound is indicative of lower rolling resistance.

25      Tangent  $\delta$  at room temperature data may be used to predict the dry traction of a tread rubber compound. An increase in this data corresponds to an increase in dry traction. As a predictor of snow traction, lower 100% modulus at -5°C when compared to a control compound indicates increased snow traction.

- With these viscoelastic properties, one can predict that high density metal oxide fillers are capable of producing consistently better rolling resistance for tire tread compounds while maintaining or improving wet traction, as compared with controls which contain carbon black or silica as reinforcement fillers.
- 5 Prediction of dry traction using viscoelastic indicators is no less than slightly lower than such controls. Prediction of cold traction using dynamic and static modulus values is better than the controls.

While not being limited to a particular theory, the use of high density metal oxide fillers in rubber compounds addresses a problem that conventional fillers have, namely: the effects of a competition of enthalpy vs. entropy in macromolecular systems. As identified by Louis F. Gatti in "Viscoelasticity: A Minimization Balance of Enthalpy and Entropy" Paper No. 31, Rubber Division 133<sup>rd</sup> Meeting of the American Chemical Society in Dallas, Texas, USA, April 19-22, 1988, polymer systems are apt to take a "wrong turn" in configuration at high energy levels. Local entropy is reduced by reducing the number of possible configurations, which increases the energy level of the polymer system. With more "wrong turns", higher energy levels result. It was hypothesized that hindrance effects were related to filler density.

In this invention, the partial or total replacement of conventional fillers with a high density filler results in improved physical properties of the rubber compound. In this manner and quite unexpectedly, use of a high density metal oxide filler will improve both wet traction and rolling resistance of tire tread rubber compounds.

25 Fillers

The vulcanizable rubber compositions, vulcanizates, and tire components of this invention may include additional fillers such as, but not limited to, carbon black and inorganic fillers.

In preferred embodiments, especially where the vulcanizable rubber compositions are employed in the manufacture of tire treads, a tread-grade carbon black is employed. The tread-grade carbon blacks are typically characterized by higher surface area and medium to high structure (*i.e.*, higher DBP). Tread-grade

carbon blacks include, but are not limited to, those classified under ASTM D-1765 as N-100 Series, N-200 Series, and N-300 Series. Alternatively, tread-grade carbon blacks include those that have an NSA multipoint surface area pursuant to ASTM D-6556 of about 60 to about 150 m<sup>2</sup>/g, preferably in excess of 65 m<sup>2</sup>/g, preferably in excess of 70 m<sup>2</sup>/g, even more preferably in excess of 75 m<sup>2</sup>/g, and even more preferably in excess of 80<sup>2</sup>/g. Alternatively, tread-grade carbon blacks include those that have a DBP No. pursuant to ASTM D-2414 of about  $65 \times 10^{-5}$  m<sup>3</sup>/kg about  $160 \times 10^{-5}$  m<sup>3</sup>/kg, preferably in excess of about  $75 \times 10^{-5}$  m<sup>3</sup>/kg, more preferably in excess of about  $85 \times 10^{-5}$  m<sup>3</sup>/kg, and even more preferably in excess of about  $95 \times 10^{-5}$  m<sup>3</sup>/kg.

The inorganic fillers may include silica, aluminum hydroxide, magnesium hydroxide, and clays (hydrated aluminum silicates). The optional organic fillers includes carbon black.

Useful silica (silicon dioxide) includes wet-process, hydrated silica produced by a chemical reaction in water, and precipitated as ultrafine spherical particles. These particles strongly associate into aggregates that in turn combine less strongly into agglomerates. The surface area, as measured by the BET method, gives the best measure of the reinforcing character of different silicas. Useful silicas preferably have a surface area of about 32 to about 400 m<sup>2</sup>/g, preferably about 100 to about 250 m<sup>2</sup>/g, preferably about 150 to about 220 mg<sup>2</sup>/g. The pH of the silica filler is generally about 5.5 to about 7 and preferably about 5.5 to about 6.8. Commercially available silicas include Hi-Sil™ 215, Hi-Sil™ 233, and Hi-Sil™ 190 (PPG Industries; Pittsburgh, Pennsylvania). Useful commercial grades of different silicas are also available from other sources including Phone Poulenc.

Useful aluminum hydroxide fillers include any aluminum hydroxide filler including those that have conventionally been employed to reinforce rubber compositions and tire components. Aluminum hydroxide filler preferably has an average diameter of about 20 nanometers (nm) to about 2,000 nm, more preferably from about 25 nm to about 1,000 nm or smaller, and even more preferably from about 30 nm to about 50 nm. Useful aluminum hydroxide

preferably has a BET specific surface area of from about 0.5 to about 500 m<sup>2</sup>/g, more preferably from about 1 to about 400 m<sup>2</sup>/g, and even more preferably from about 2 to about 300 m<sup>2</sup>/g. Aluminum hydroxide filler may be treated with various surface treating agents. Non-limiting examples of surface treating agents 5 include organic treating agents such as fatty acids and alcohols, and inorganic dispersants such as coupling agents and fatty acid metal salts. Useful aluminum hydroxide filler is commercially available from a number of sources including that available under the tradenames Hygilite™ (Showa Dendo K.K.; Japan), Baikalox™ (Baikowski Chimie; France), and RF22™ (Sumitomo Chemical Co.: Japan).

10 A coupling agent may optionally be added when an inorganic filler such as silica is used. Coupling agents include those compounds that are believed to react with both the rubber and the inorganic filler. One coupling agent conventionally used is bis-[3(triethoxysilyl) propyl]-tetrasulfide, which is commercially available under the tradename SI69 (Degussa, Inc.; New York, New 15 York). Other coupling agents include bis-[3(triethoxysilyl) propyl]-disulfide, which is commercially available under the tradename Silquest™ (Witco; Greenwich, Connecticut), mercapto propyl alkoxy silane, which is commercially available under the tradename Ciptane™ (Dow Corning; Midland, Michigan), and dithio dipropionic acid or carboxylic acid disulfides, which are commercially available 20 from Aldrich Chemical Company. In general, these coupling agents should be used in an amount from about 0.1 to 20 % by weight based upon the weight of the inorganic filler.

Shielding and dispersing agents, which prevent or alleviate the agglomeration of inorganic filler particles such as silica, may also be used. 25 Typically, these agents react or interact with the filler. Exemplary dispersing or shielding agents include silanes, amines, diols, polyethers, amides, and sugar fatty acid esters. U.S. Patent Nos. 5,719,207, 5,780,538, 5,717,022, and EP 0890606 are incorporated herein by reference in this regard. Specific examples of these 30 agents include sugar, fatty acids such as sorbitan fatty acids which are available from BASF (Mount Olive, New Jersey), and octyl triethoxy silane, which is available from Dow Corning (Midland, Michigan). Generally, these shielding or dispersing agents may be used in an amount from about 0.1 to about 20% by

weight based on the weight of the inorganic filler. In preferred embodiments, the coupling agents, shielding agents, and dispersing agents may be used in combination.

In a preferred embodiment, especially where the vulcanizable rubber compositions are employed in the manufacture of tire treads, the vulcanizable compositions, as well as the vulcanizates and tire treads resulting therefrom, will include from about 1 to about 80 phr metal oxide filler, from about 1 to about 100 phr tread-grade carbon black, and from about 0 to about 100 phr inorganic filler. Preferably, the vulcanizable compositions will include from about 2 to about 50 phr metal oxide filler, from about 10 to about 90 phr tread-grade carbon black, and from about 10 to about 90 phr inorganic filler. Even more preferably the vulcanizable compositions will include from about 3 to about 20 phr metal oxide filler, from about 20 to about 80 phr tread-grade carbon black, and from about 20 to about 80 phr inorganic filler.

In order to demonstrate the practice of the present invention, the following examples have been prepared and tested. The examples should not, however, be viewed as limiting the scope of the invention. The claims will serve to define the invention.

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## EXAMPLES

### General Experimental Testing Procedures

#### 1. Modulus, Tensile Strength and Elongation at Break

Modulus, Tensile Strength (Stress at Maximum Strain) and Elongation at Break are measured generally according to ASTM D 412 (1998) method B. Vulcanized rubber test specimens are cut into the shape of a ring, using a D412 B Type 1 die. The measurements for the above properties are based on the original cross sectional area of the test specimen. An instrument equipped to produce a uniform rate of grip separation, such as an Instron tensile tester, with a suitable dynamometer and an indicating or recording system for measuring applied force is used in conjunction with a measurement of extension of the test specimen. Modulus (100% (M100) and 300% (M300)), tensile strength (TB) and elongation (EB) are calculated according to the calculations set forth in ASTM D412 (1998).

2. Rebound

Rebound, the resilience of a rubber sample based on the ratio of returned to delivered energy, is measured generally according to test method ASTM D1054-91 (2000). A rubber sample is milled and cured according to ASTM 5 D 1054, using the mold specified. The cured sample is then coated with talc, prior to conditioning. The sample is conditioned in an oven set at the requested temperature for approximately 1 hour. The conditioned sample is placed into a Zwick type rebound tester, such that a pendulum is swung against the sample, and the angle which it bounces back is measured. The percentage rebound is 10 calculated using the equation found in D1054-91(2000).

3. MTS

MTS measures the dynamic spring rate and damping characteristics of a rubber sample. The sample is subjected to a vibration at a specified load, frequency, temperatures and deflection. The elastic spring rate ( $K'$ ) and damping 15 coefficient (C) are then determined using the following formulae:

$$F(t) = K' x + C x^*$$

where:

$F(t)$  = applied force

$K'$  = elastic spring rate (lb/in)

20  $x$  = displacement (inch)

$C$  = damping coefficient (lb sec/in) or the per cycle  
dissipation energy

$x^*$  = change in displacement with respect to time

The viscous spring rate ( $K'$ ) can be calculated by using the damping 25 coefficient:

$$II. \quad K' = 2 \pi / f C$$

where:

$f$  = the frequency of the vibration

Additionally,  $\tan \delta$  can be calculated from the spring rate data, using 30 the following formula:

$$\tan \delta = K''/K'$$

Rubber samples of 2.22 cm in diameter and 1.90 cm in height are cured in an MTS mold. An MTS 830 elastomer test system is used in conjunction with a 458.20 micro console and an MTS 409.80 temperature controller to analyze the test specimen. For the following Examples, the samples were preconditioned by 5 cycling at the set frequency and temperature for a period of 2 minutes. The testing conditions, at various temperatures, used for the following Examples are shown in Table 1.

Table 1				
MTS Test Conditions	0°C	RT	50°C	65°C
Preload (kg)	22.7	11.3	4.5	4.5
Frequency (Hz)	10	10	10	10
Deflection (%)	2	5	5	5

10 General Experimental Materials Examples

In these Examples, a high density metal oxide filler is used as a partial replacement to conventional reinforcing rubber fillers.

15 For the following Examples, bismuth trioxide is used to replace varying amounts of carbon black in both carbon black filled and carbon black and silica filled rubber compounds.

Examples 1 and 2 and Comparative Example A

Comparative Example A (Comp. A) was representative of a carbon black filled tread compound. Experimental Examples 1 and 2 (Exp. 1 and Exp. 2) were modified versions of this compound. In Example 1, 10 phr of carbon black was 20 replaced by an equivalent amount of bismuth trioxide. In Example 2, 10 phr of carbon black is replaced with 17 phr of bismuth trioxide, while additional aromatic oil is also added to the composition:

25 Each of Comparative Example A, and Experimental Examples 1 and 2 were mixed in three mix stages. For the first non-productive mix stage, the ingredients were mixed for approximately 180 seconds to a temperature of about 177°C. The rubber compound was then removed from the mixer, and was subsequently mixed with additional filler in a second non-productive mix stage.

During this second mix stage, the ingredients were mixed for approximately 110 seconds, to a temperature of about 160°C. The resulting rubber composition was then mixed with sulfur curatives, accelerators, and additional anti-oxidants to a maximum temperature of about 99°C, for about 95 seconds, in a final, productive  
5 mix stage.

The rubber compositions of this set of Examples were comprised of ingredients listed in Table 2.

Table 2				
Materials	Comp.A	Exp. 1	Exp. 2	
Masterbatch #1				
Emulsion SBR <sup>1</sup>	137.5	137.5	137.5	
Processing Oil <sup>2</sup>	17	17	22	
Wax <sup>3</sup>	1	1	1	
Carbon Black <sup>4</sup>	65	55	55	
Bi <sub>2</sub> O <sub>3</sub> <sup>5</sup>	0	10	17	
Zinc Oxide	1.7	1.7	1.7	
Stearic Acid	1	1	1	
Masterbatch #2				
Carbon Black <sup>4</sup>	20	20	20	
Final				
Sulfur	1.8	1.8	1.8	
Antidegradant <sup>5</sup>	0.95	0.95	0.95	
DPG <sup>6</sup>	0.4	0.4	0.4	
TBBS <sup>7</sup>	1.15	1.15	1.15	
MBTS <sup>8</sup>	0.4	0.4	0.4	

- 10           <sup>1</sup> Emulsion polymerization prepared, oil extended styrene/butadiene rubber available as Ameripol Synpol 1712H, from Ameripol-Synpol Corp.;  
              <sup>2</sup> Aromatic processing oil, available as Textract 2205 from Texaco;  
              <sup>3</sup> Available as Okerin 1875 from Astor Wax Corp.;  
              <sup>4</sup> N234 type carbon black;  
              <sup>5</sup> Bismuth Trioxide having a specific gravity of approximately 8.3, available from The Sheperd Chemical Company;,  
              <sup>6</sup> Available as Santoflex 13 from Flexsys;  
              <sup>7</sup> Perkacit DPG, available from Flexsys;  
              <sup>8</sup> Santocure TBBS, available from Flexsys;  
              <sup>9</sup> Perkacit MBTS, available from Flexsys;

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Each of the Examples was then vulcanized at a temperature of about 170°C for about 15 minutes. The physical properties for the resulting vulcanized  
25 rubber compositions are shown in the following Table 3.

	Comp. A	Exp. 1	Exp. 2
MTS			
Tan δ @ 0°C	0.452	0.448	0.456
K' @ RT	1204	1224	1163
Tan δ @ RT	0.347	0.349	0.347
Tan δ @ 65°C	0.338	0.302	0.288
Stress/Strain			
M300 @ RT	7.3	7.9	7.6
TB @ RT	17	18.8	17.6
EB @ RT	570	552	539
M100 @ -5°C	4.05	3.53	3.36
Zwick Rebound, %			
0°C	19.4	20.2	20.4
RT	27.1	30.8	30.9
65°C	36.7	41.5	42.6
100°C	41.9	49.8	51.1

As a predictor of wet traction, the comparison of tangent δ (tan δ) at

- 5      0°C results indicate that the replacement of bismuth trioxide in a carbon black filled tread compound will not significantly affect the wet traction performance of this compound. Tangent δ data derived from MTS testing is also useful for predicting rolling resistance, as explained above. Tangent δ at 65°C for the modified compositions decreased, indicative of a lower rolling resistance.
- 10     These results, illustrated in Figure 1, which is a plot of tangent δ versus temperature, are surprising in that improving wet traction of a rubber compound usually results in a negative increase in rolling resistance, or vice versa.

These predictions are also supported by the % rebound data. As a percentage, rebound of the modified rubber compositions at 0°C, also a predictor of wet traction remained essentially equivalent to the control compound, Comparison Example A. Percent Rebound at 65°C, an indicator of rolling resistance, increased when carbon black was replaced equivalently with bismuth trioxide. Such an increase corresponds to a decrease in rolling resistance of the tread compound. The increase in percent rebound at 65°C was even greater for

- 15     Example 2, in which carbon black was replaced with a disproportionately high amount of bismuth trioxide. These results are further displayed in Figure 2, in
- 20     which the effect of the reduced carbon black loading on rolling resistance is shown.

which the percent rebound at various temperatures of Exp. 1 and Exp. 2 are compared to the percent rebound of the control.

Examples 1 and 2 also show that 100% modulus at -5°C were lower than for Comparative Example A. Lower 100% modulus at -5°C indicates 5 improved cold traction for the tread compound. Additionally, the higher tangent  $\delta$  at room temperature values for the Examples 1 and 2 indicate improved dry traction of those compounds when compared to the control. The remaining stress strain data contained in Table 3 indicates that these properties were not significantly affected by the replacement and addition of bismuth trioxide to the 10 tread rubber composition.

#### Examples 3 and 4 and Comparative Example B

Comparative Example B is a tread compound containing both carbon black and silica as reinforcing fillers. In Example 3, when compared to Comparative Example B, the amount of carbon black used is reduced by 5 phr, and 15 6 phr of bismuth trioxide is added to the rubber composition. In Example 4, the amount of carbon black is reduced by 8 phr comparatively, and the amount of bismuth trioxide added to the composition is 10 phr. The softener content is not adjusted in either of Examples 3 or 4.

The compositions in this set of Examples were mixed in four mix stages. 20 For the first non-productive mix stage, the ingredients were mixed for approximately 280 seconds to a temperature of about 177°C. The rubber compound was then removed from the mixer, and was subsequently mixed with additional filler in a second non-productive mix stage. During this second mix stage, the ingredients were mixed for approximately 200 seconds, to a temperature 25 of about 143°C. A third, non-productive mix stage follows, in which no new ingredients were added to the rubber composition. The rubber compound is mixed at about 143°C, for approximately 90 seconds. During the fourth and final, productive mix stages, the rubber composition was then mixed with sulfur curatives, accelerators, and additional anti-oxidants to a maximum temperature of 30 about 99°C, for about 90 seconds.

The rubber compositions of this Example are comprised of ingredients listed in Table 4.

**Table 4**

Materials	Comp.B	Exp. 3	Exp. 4
<b>Masterbatch #1</b>			
Emulsion SBR <sup>1</sup>	116.88	116.88	116.8
BR <sup>2</sup>	15	15	8
Processing Oil <sup>3</sup>	3.6	3.6	15
Wax <sup>4</sup>	0.2	0.2	3.6
Carbon Black <sup>5</sup>	28.75	23.75	0.2
Silica <sup>6</sup>	40	40	20.75
Bi <sub>2</sub> O <sub>3</sub> <sup>7</sup>	0	6	40
<b>Zinc Oxide</b>	2.5	2.5	10
	1	1	2.5
Stearic Acid	0.95	0.95	1
Antidegradants <sup>8</sup>	5.87	5.87	0.95
Coupling Agent <sup>9</sup>			5.87
<b>Masterbatch #2</b>			
Carbon Black <sup>5</sup>	20	20	20
<b>Remill</b>	-----	-----	-----
<b>Final</b>			
Sulfur	2.3	2.3	2.3
DPG <sup>10</sup>	0.6	0.6	0.6
CBS <sup>11</sup>	0.7	0.7	0.7
MBTS <sup>12</sup>	0.7	0.7	0.7

5           <sup>1</sup> Emulsion polymerization prepared, oil extended styrene/butadiene rubber, available as Ameripol Synpol 1721 from Ameripol-Synpol Corp.;

10           <sup>2</sup> Butadiene rubber available as Kumho BR01 from Korea Kumho Petrochemical Co., LTD.;

15           <sup>3</sup> Aromatic processing oil, available as Sundex 790T from Sun Refining & Marketing Co.;

<sup>4</sup> Available as Okerin 1875 from Astor Wax Corp.;

<sup>5</sup> N234 type carbon black;

<sup>6</sup> VN3 type silica available from Degussa AG.

<sup>7</sup> Bismuth Trioxide having a specific gravity of approximately 8.3, available from The Sheperd Chemical Company.;

<sup>8</sup> Of the dialkyl paraphenylenediamine type;

<sup>9</sup> Bis (3-triethoxysilylpropyl) disulfide, available as Si75 from Degussa Corp.;

<sup>10</sup> Perkacit DPG, available from Flexsys;

<sup>11</sup> Santocure CBS, available from Flexsys;

<sup>12</sup> Perkacit MBTS, available from Flexsys;

20           Each of the rubber compositions was vulcanized at a temperature of about 170°C for about 15 minutes. The physical properties for the resulting vulcanized rubber compositions are shown in the following Table 5.

	Comp. B	Exp. 3	Exp. 4
MTS			
Tan δ @ 0°C	0.433	0.490	0.538
K' @ RT	1679	1637	1561
Tan δ @ RT	0.332	0.331	0.334
Tan δ @ 65°C	0.294	0.274	0.267
Stress/Strain			
M300 @ RT	11.3	10.4	10.5
TB @ RT	17.4	18.1	19.3
EB @ RT	433	467	483
M100 @ -5°C	10.5	10.1	9.7
Zwick Rebound, %			
0°C	12.4	11.8	11.2
RT	22.8	24.0	24.6
65°C	38.4	41.6	43.7
100°C	48.0	51.6	53.0

The tangent δ at 0°C from Table 4 shows an increase in values for

- 5 Examples 3 and 4 when compared to Example B. This trend indicates that the replacement of bismuth trioxide for a portion of carbon black comprising a carbon black and silica filled tread compound results in an increase in wet traction for that tread compound. As a predictor of rolling resistance, tangent δ at 65°C for the modified compositions decreased, indicating a lower rolling resistance.

- 10 These results, illustrated in Figure 3, which is a plot of tangent δ versus temperature, are quite unexpected.

These predictions are also supported by the % rebound data. As a percentage, rebound of the modified rubber compositions at 0°C, also a predictor of wet traction, decreased for Examples 3 and 4, when compared with Example B.

- 15 Percent rebound at 65°C, increased when carbon black was replaced equivalently with bismuth trioxide, indicating a decrease in rolling resistance. These results are illustrated in Figure 4, in which the percent rebound at various temperatures of Examples 3 and 4 are compared to the percent rebound for Example B.

- 20 Additionally, Examples 3 and 4 also show that 100% modulus at -5°C results were lower than Comparative Example B, indicating improved cold traction for the tread compound. Also, the higher tangent δ at room temperature values for the experimental examples indicate improved dry traction of those compounds

when compared to the control. The remaining stress strain data contained in Table 5 indicates as well, that these properties were not significantly affected by the replacement and addition of bismuth trioxide to the tread rubber composition. Several aspects of this invention are also disclosed in U.S. Serial No. 09/840,288, 5 which is incorporated herein by reference.

Various modifications and alterations that do not depart from the scope and spirit of this invention will become apparent to those skilled in the art. This invention is not to be duly limited to the illustrative embodiments set forth herein.